



TITLE:

Controlled Graft Polymerization on Silicon Substrate by the Combined Use of the Langmuir-Blodgett and Atom Transfer Radical Polymerization Techniques (ORGANIC MATERIALS CHEMISTRY-Polymeric Materials)

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CITATION:

Ejaz, Muhammad ...[et al]. Controlled Graft Polymerization on Silicon Substrate by the Combined Use of the Langmuir-Blodgett and Atom Transfer Radical Polymerization Techniques (ORGANIC MATERIALS CHEMISTRY-Polymeric Materials). ICR Annual Report 1998, 4: 30-31

ISSUE DATE:

1998-03

URL:

<http://hdl.handle.net/2433/65153>

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# Controlled Graft Polymerization on Silicon Substrate by the Combined Use of the Langmuir-Blodgett and Atom Transfer Radical Polymerization Techniques

Muhammad Ejaz, Shinpei Yamamoto, Kohji Ohno, Yoshinobu Tsujii, Takeshi Fukuda and Takeaki Miyamoto

The atom transfer radical polymerization technique using the copper/ligand complexes was applied to the graft polymerization of methyl methacrylate on the Si wafer on which the monolayer of the initiator, 2-(4-chlorosulfonylphenyl) ethyl trimethoxysilane, was immobilized by the Langmuir-Blodgett technique. Atomic force microscopic and ellipsometric studies revealed that the polymerization with an additional initiator afforded a homogeneous graft layer, the thickness of which increased proportionally to the number-average molecular weight of the narrow-polydispersity homopolymers produced in the solution. This suggests that the graft polymerization is successfully controlled by the Cu/ligand complexes in the same way as the solution polymerization.

**Keywords:** Surface modification / Monolayer / Immobilization / Controlled radical polymerization / Graft layer / Ellipsometry

Recently much interest has been directed towards new ways to modify surfaces of solid substrates for potential applicability. Graft polymerization starting with the initiating sites fixed on the surface is one of the most effective and versatile methods for such surface modification. However, it is usually very difficult to control molecular weight, molecular weight distribution, and surface density of graft chains. We attempted to precisely control all these three parameters by the combined use of two independent techniques: one is the Langmuir-Blodgett (LB) technique to provide a well organized set of initiating sites on the substrate, and the other is the atom transfer radical polymerization (ATRP) technique using copper(Cu) /ligand(L) complexes<sup>1)</sup> to achieve a con-

trolled graft polymerization. ATRP is one of the several techniques of controlled/"living" radical polymerization that has been attracting much attention as a new route to well-defined polymers with low polydispersities.<sup>2)</sup>

In this work, we have examined the graft polymerization of methyl methacrylate (MMA) by ATRP on an initiator-fixed substrate. 2-(4-Chlorosulfonylphenyl) ethyl trimethoxysilane (CTS) was used as an initiator which can be immobilized on an oxidized silicon substrate; the Cl atom of a chlorosulfonyl group (-SO<sub>2</sub>Cl) is easily abstracted by the Cu/L complex, and the produced -SO<sub>2</sub>\* radical initiates the radical polymerization.

## Immobilization of Initiator

Figure 1 schematically illustrates the immobilization

## ORGANIC MATERIALS CHEMISTRY — Polymeric Materials —

### Scope of research

Basic studies have been conducted for better understandings of the structure/property or structure/function relations of polymeric materials and for development of novel functional polymers. Among those have been the studies on (1) the syntheses and properties of cellulose- and oligosaccharide-based functional polymers, e.g., bio-degradable polymers, liquid crystals and polymers of well-defined structure having pendant oligosaccharides, (2) the structure of polymer gels, ultrathin films and polymer alloys, and (3) the syntheses of new types of block and graft copolymers and fullerene(C<sub>60</sub>)-including polymers.



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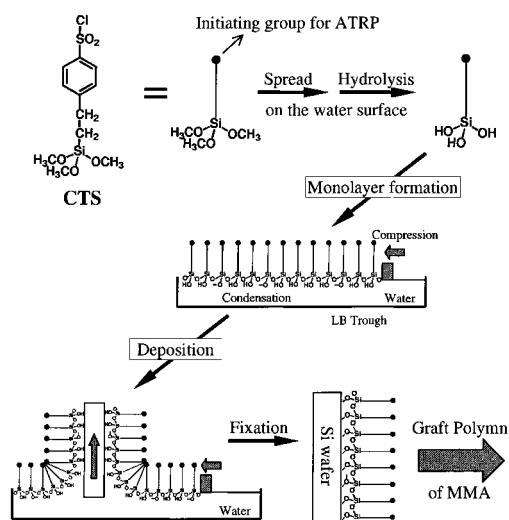
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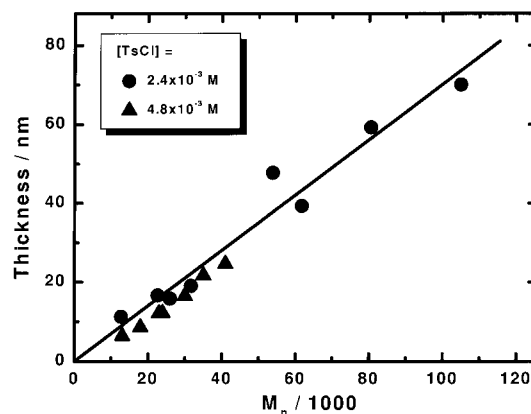
**Figure 1** Schematic illustration of the immobilization process of the initiator by the LB technique.

process of the initiating groups. CTS was spread from a chloroform solution on the clean water surface in a Langmuir trough, where methoxysilyl groups ( $\equiv\text{Si}-\text{OCH}_3$ ) of CTS were presumably hydrolyzed to silanol groups ( $\equiv\text{Si}-\text{OH}$ ). The surface pressure ( $\pi$ ) – occupied area ( $A$ ) isotherm of CTS suggests the formation of a monolayer on the water surface. When  $\pi$  was kept 10 mN/m at which the isotherm gave the steepest rise, the occupied area decreased by about 10%, approaching a constant value. This initial decrease in  $A$  might be due to the polycondensation between silanol groups formed by the hydrolysis of CTS on the water surface.

After the surface monolayer was annealed for 30 min at  $\pi = 10$  mN/m, it was transferred by the lifting-up method onto the oxidized silicon substrate. The transfer ratio, defined as the difference in the water surface area before and after the deposition divided by the substrate surface area, was approximately unity, indicating successful deposition and the formation of a Z-type monolayer film. Thermal treatment of thus obtained substrate at 110 °C for 20 min was carried out to promote the reaction of unreacted silanol groups of CTS with silanol groups on the silicon substrate, forming covalent bonds between the CTS film and the substrate. The atomic force microscopic (AFM) observation suggests that homogeneous immobilization of CTS has been achieved.

### Controlled Graft Polymerization

The graft polymerization on the initiator-fixed substrate was carried out for various periods at 90 °C in a degassed diphenyl ether solution of CuBr, 4,4'-di-n-heptyl-2,2'-bipyridine (ligand), MMA, and an additional initiator, *p*-toluenesulfonyl chloride (TsCl). The polymerization without TsCl gave free homopolymers with high polydispersities ( $M_w/M_n > 3$ ) like the conventional radical polymerization. This is presumably because the



**Figure 2** Relationship between graft-layer thickness and  $M_n$  of free homopolymers produced in solution.

concentration of initiator in the solution was much too low to control the polymerization. In fact, addition of an appropriate amount of TsCl as a free initiator in solution brought about well-controlled polymerization; the free homopolymers had relatively low polydispersities and the  $M_n$  values were proportional to the monomer conversion with the slope which is very close to the theoretical values defined by the feed concentration of TsCl. This indicates that the number of polymer chains is kept constant during the polymerization and hence transfer and termination reactions are negligible.

The AFM observation revealed that a homogeneous polymer layer was formed on the substrate. We confirmed by repeatedly rinsing the substrate with chloroform that the polymer chains were not physically adsorbed but chemically anchored onto the substrate. Ellipsometric study revealed that the thickness of the grafted layer increased with time, and the polymerization with a lower concentration of TsCl gave a thicker layer with the same polymerization time. Since the molecular weight of the polymer grafted on the substrate should be somehow correlated to that of the homopolymer produced in the solution, the graft layer thickness was plotted against the  $M_n$  values of the homopolymer in the solution (Figure 2). A proportional relationship was obtained between them, and the slope of the line was independent of the concentration of TsCl. This strongly suggests that the  $M_n$  of the graft polymer is almost equal or at least proportional to that of the homopolymer and the graft density is constant during the course of polymerization. Thus, it was concluded that the graft polymerization is controlled by the Cu/ligand complexes in the same way as the solution polymerization.

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